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Supplementary Material Available: Spectral and analytical data for **4**, **2**, and **1** (2 pages). Ordering information is given on any current masthead page.

An Ethylene Complex of Vanadium: Synthesis, Structure, and Reactivity of Cyclopentadienyl-bis(trimethylphosphine)(ethylene)vanadium(I)

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Although olefin complexes of the early transition metals are frequently named as intermediates in catalytic reactions such as olefin polymerization and hydrogenation,[1] very few complexes have actually been isolated, especially for the 3d-metals. For Ti the sole representative of this class of compounds is $(\eta\text{-}C_5Me_5)_2Ti(ethylene)$,[2] while for V only two compounds are fully characterized: $Cp_2V(EtO_2CCH{=}CHCO_2Et)$[3] and $V(CO)_4[PPh_2(2\text{-}alkenylphenyl)]$,[4] the latter stabilized by the chelate effect. Here we wish to report a simple olefin complex of V(I), $CpV(\eta^2\text{-}ethylene)(PMe_3)_2$, with some aspects of its reactivity.

When $CpVCl_2(PMe_3)_2$[5] (**1**) is reacted with 1 mol of 1,4-bis(bromomagnesio)butane in THF at 0 °C, the ethylene complex $CpV(ethylene)(PMe_3)_2$ (**2**) can be isolated in 38% yield, instead of a possibly anticipated vanadiocyclopentane product. The blue $CpVCl(PMe_3)_2$[6] was observed as an intermediate in the reaction.[7] **2** can also be obtained, in 49% overall yield, from the reaction of $CpVCl(PMe_3)_2$ (produced by reduction of **1** with 1 mol of Na/Hg) with 0.5 mol of the diGrignard. Thus it seems likely that **2** is not formed by elimination of ethylene from a vanadiocyclopentane intermediate but by rearrangement of a 1,4-divanadiobutane complex (eq 1). This behavior appears to be

$$\mathbf{1} \xrightarrow[THF]{Na/Hg} CpVCl(PMe_3)_2 \xrightarrow[THF,\ 0\ °C]{{}^1/_2(BrMg)_2(CH_2)_4} {}^1/_2[Cp(PMe_3)_2VCH_2(CH_2)_2CH_2V(PMe_3)_2Cp] \rightarrow CpV(ethylene)(PMe_3)_2 \quad (1)$$
$$(\mathbf{2})$$

unprecedented for 1,4-dimetallabutanes. However, recently the production of ethylene from reduction of 1,4-dibromobutane by a nickel tetraazaannulene complex was reported.[9] One of the mechanisms suggested there (a concerted internal electron-transfer reaction) may well be applicable in our case.

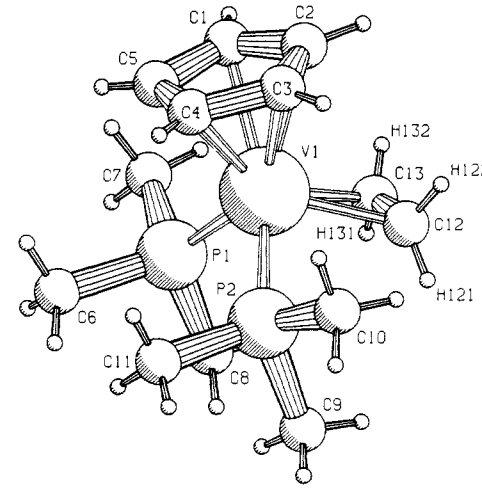

Figure 1. Molecular structure of $CpV(\eta^2\text{-}ethylene)(PMe_3)_2$ (**2**). Selected structural parameters are as follows: V(1)-P(1) = 2.429 (1) Å, V(1)-P(2) = 2.427 (1) Å, V(1)-C(12) = 2.153 (3) Å, V(1)-C(13) = 2.173 (3) Å, C(12)-C(13) = 1.365 (5) Å, ∠P(1)-V(1)-P(2) = 95.97 (3)°, ∠C(12)-V(1)-C(13) = 36.8 (1)°.

2 is a green crystalline paramagnetic (by NMR) 16-electron high spin complex, extremely air sensitive, but thermally stable in solution at 0 °C. An X-ray structure determination[10] shows (Figure 1) that **2** has a simple piano-stool geometry with the phosphine ligands in eclipsed conformation. The V-C(ethylene) distances are close to those in $Cp^*_2Ti(ethylene)$ (2.160 (4) Å^2), but the amount of π-backdonation (and concomitantly the amount of metallacyclopropane character) is much smaller than in the latter compound. This can be seen from both the ethylene C-C distance and the sharp dihedral angle α between the two planes through each of the two CH_2 groups (both increase with increasing metallacyclopropane character[11]). **2**: C(12)-C(13) = 1.365 (5) Å, α = 47. (3)°; $(C_5Me_5)_2Ti(ethylene)$:[2] C-C = 1.438 (5) Å, α = 70. (4)°; ethylene:[12] 1.337 (2) Å, α = 0°. The relatively small amount of π-backdonation into the ethylene π^*-orbital in **2** (despite formally being a d^4-species) may be caused by competition from the two phosphine ligands.

The ethylene complex **2** exhibits a wide range of reactivity. With (hard or soft) Lewis bases displacement of the ethylene ligand can occur. E.g., **2** reacts with CO, diphenylacetylene, or 2,2′-bipyridine to form $CpV(CO)_2(PMe_3)_2$,[13] $CpV(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)_2$, and the paramagnetic $CpV(bpy)PMe_3$, respectively. Thus through **2** various CpV(I)-species that do not contain CO ligands can be synthesized under mild conditions (0 °C). Apart from CpV(arene) species,[14] all CpV(I) compounds known so far contain at least one carbonyl ligand. The ethylene ligand is retained in reaction with CO_2, where the 2-oxavanadacyclo-3-pentanone $CpV(\eta^1\text{-}O_2CCH_2CH_2)PMe_3$ (ν_{CO} = 1565 cm^{-1}) is formed. Oxidative addition to the low valent metal center can also be observed: **2** reacts with diphenyldisulfide to give the insoluble dimeric V(III) species $[CpV(\mu\text{-}SPh)_2]_2$.[15] **2** is moderately active in the catalytic dimerization of olefins. For example, 38 mol/mol V of 1-hexene is transformed into $C_{12}H_{24}$ (three isomers, GCMS M$^+$ = 168) in 48 h (1-hexene, room temperature).

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(7) V(III) in **1** is reduced to V(II) by β-H containing alkyl Grignards like EtMgBr and *n*-PrMgBr, yielding $CpVX(PMe_3)_2$ (X = Cl, Br). Reaction of **1** with 2 mol of *n*-PrMgBr in THF produces a poorly soluble brown material. No formation of **2** was observed, making THF as an ethylene source[8] for **2** unlikely.
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(10) **2** crystallizes in the orthorhombic space group *Pbca*, *a* = 12.351 (3) Å, *b* = 15.526 (4) Å, *c* = 16.948 (3) Å (140 K), *Z* = 8. Reflections (2474) with $1.2° \le \theta \le 26.0°$ were considered observed. All hydrogen atoms were located from the Fourier difference map and refined isotropically. R = 0.035, R_w = 0.041 ($w = 1/\sigma^2(F)$) for 254 refined parameters.
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Olefin dimerization has been observed for the $(C_5Me_5)Ta(olefin)Cl_2$ system[16] but not for the Ti complex $(C_5Me_5)_2Ti(ethylene)$.[2] Full reactivity of **2** will be reported elsewhere.

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Supplementary Material Available: Experimental details and spectral data for all compounds, crystal data, and lists of positional and thermal parameters (11 pages); listing of observed and calculated structure factors for **2** (13 pages). Ordering information is given on any current masthead page.

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Stereochemistry of the Biosynthesis of *sn*-2,3-*O*-Diphytanyl Glycerol, Membrane Lipid of Archaebacteria *Halobacterium halobium*

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One of the most striking and characteristic differences of archaebacteria from other evolutionary diverged eubacteria and eukaryotes is the stereostructure of a unit lipid of the cell membrane, *sn*-2,3-*O*-dialkylated glycerol, having, when present, a polar head group on the *sn*-C-1 position.[1,2] Eubacteria and eukaryotic cells mostly contain antipodal *sn*-1,2-*O*-diacyl glycerol as a major lipid. Biochemical pathway concerning to this intriguing stereochemical divergence has yet to be uncovered. This paper deals with the cryptic stereochemistry of glycerol incorporation into the archaebacterial lipid studied by tracing stereospecifically deuteriated glycerol and demonstrates for the first time that stereochemical inversion takes place at the C-2 position of glycerol.

Biosynthetic studies on the lipid and related metabolite have been reported recently by using two classes of archaebacterial strains, i.e., halophilic *Halobacterium cutirubrum*[3] and extreme acidothermophile *Sulfolobus* sp. (*Caldariella acidophila*).[4] The latter actually contains an interesting 72-membered ring structure of biphytanyl diglycerol tetraether as a principal membrane lipid which can also be classified in the *sn*-2,3-*O*-dialkylated glycerol family.[5] In either case, glycerol was reported to be incorporated efficiently into the membrane lipid,[3,4] and all the hydrogens of glycerol except hydroxyl groups were reported to be retained in the biosynthesis of the lipid in *Sulfolobus* sp.[3] If, as emphasized previously,[2,4,6] formation of the ether linkages might take place between glycerol or its derivative and prenyl pyrophosphate,

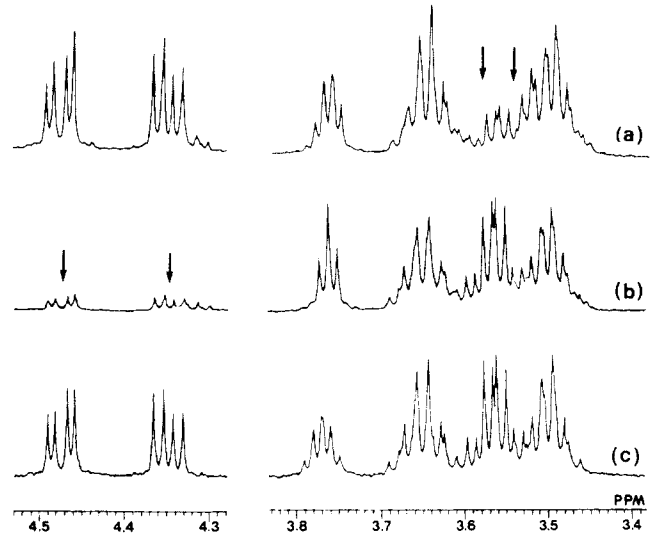

Figure 1. ^1H NMR spectra (500 MHz, $CDCl_3$ solvent, TMS reference) of benzoylated lipids: (a) the lipid obtained by feeding of (*S*)-[1,1-$^2H_2$]glycerol, (b) the lipid obtained by feeding of (*R*)-[1,1-$^2H_2$]glycerol, and (c) the unlabeled control.

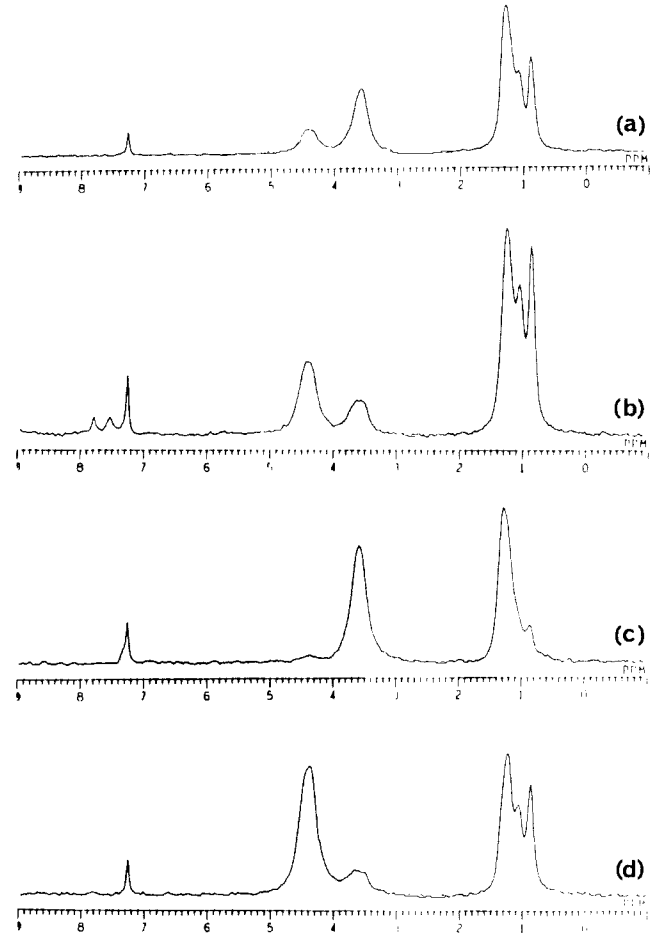

Figure 2. ^2H NMR spectra (61.48 MHz, $CHCl_3$ solvent, natural abundance ^2H signal of $CHCl_3$ was used for a chemical shift standard, δ = 7.26 ppm) of benzoylated lipids obtained by feeding of (a) racemic [1,1-$^2H_2$]glycerol, (b) (*R*)-[1,1-$^2H_2$]glycerol, (c) (*S*)-[1,1-$^2H_2$]glycerol, and (d) D-[6,6-$^2H_2$]glucose.

stereochemical inversion would not occur at the C-2 position of glycerol. Alternatively, antipodal stereochemistry might arise from stereochemically opposite phosphorylation or other activation of glycerol to the case of eubacteria or eukaryotes.

Separate feeding of chemically synthesized (*RS*)-[1,1-$^2H_2$]-glycerol, (*R*)-[1,1-$^2H_2$]glycerol, and (*S*)-[1,1-$^2H_2$]glycerol to the

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